

## **Environmental Monitoring Technologies**

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**Program:** Environmental Monitoring Technologies

**Title:** Standard Reference Materials (SRMs) and Quality Assurance Activities to Support Measurements of Organics on Air Particulate Matter less than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ )

**Authors:** S.A. Wise, J.R. Kucklick, B.J. Porter, D.L. Poster, M.M Schantz, R.O. Spatz, and R. Zeisler

**Abstract:** The Analytical Chemistry Division is collaborating with the Environmental Protection Agency to develop SRMs to support measurements of organic species in fine particulate matter (PM). This collaboration focuses on three projects: (1) establishment of an interlaboratory comparison program to assess measurement comparability, (2) development of solution SRMs for compounds of interest for PM measurements, and (3) collection of bulk  $\text{PM}_{2.5}$  for use as a future SRM. To date three interlaboratory comparison exercises have been conducted for the determination of organic contaminants and source markers in PM samples. A series of calibration solution SRMs are in progress for aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), nitro-substituted PAHs, hopanes/steranes, and  $^{13}\text{C}$ -labeled and deuterium-labeled levoglucosan.

**Purpose:** In 1997 the Environmental Protection Agency (EPA) issued new standards for air particulate matter (PM) under the national ambient air quality standards including new regulations for PM less than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ), which is the respirable PM fraction, in addition to the existing  $\text{PM}_{10}$  standards. Research recommendations have been made by the National Research Council at the request of Congress and EPA to focus on evaluating what types of particles cause detrimental health effects. To support compositional analyses and other investigations on the fine PM, quality assurance materials are necessary; however, few appropriate fine particulate materials are currently available to support this research. NIST has entered an agreement with the EPA to develop SRMs to support analytical measurements of organic constituents in  $\text{PM}_{2.5}$ , to improve interlaboratory comparability of measurements, and to provide national measurement traceability.

**Major Accomplishments:** The NIST/EPA agreement has focused on three projects with the goal of providing quality assurance and SRMs to support measurements of organic compounds in fine PM including: (1) establishment of a interlaboratory comparison program to assess measurement comparability, (2) development of solution SRMs for compounds of interest for PM measurements, and (3) collection of bulk  $\text{PM}_{2.5}$  for use as a future SRM. As part of the NIST/EPA collaboration, the Organic Speciation Working Group was formed in 2000 to assist in this effort by participating in interlaboratory comparison studies and by providing input for the development of SRMs to support these measurements. This group has participated in three interlaboratory comparison studies for the determination of polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs, alkanes (including hopanes and cholestanes), sterols, carbonyl compounds (ketones and aldehydes), acids (alkanoic and resin), phenols, and sugars in PM-related samples. Based in part on the results of these studies and input from the Organic Speciation Working Group, priorities for the development of a number of calibration solution SRMs were identified including: aliphatic hydrocarbons, PAHs, nitro-substituted PAHs,

hopanes/steranes, and  $^{13}\text{C}$ -labeled and deuterium-labeled levoglucosan (for use as internal standards). SRM 1494 Aliphatic hydrocarbons in Iso-octane was issued in early 2004. SRMs 2260a PAHs in Toluene and 1491a Methyl-substituted PAHs in Toluene, which are redesigned solutions with an expanded list of 53 PAHs and alkyl-substituted PAHs, were completed in late 2004. The remaining solution SRMs are in progress and will be completed in 2005.

Collection of a 200-g bulk sample of ultra-fine particulate matter at a site in Baltimore, MD with a high-volume sampler has been only partially successful. Two collections of 20 g each have been used to prepare an interim reference material and for distribution in the NIST/EPA interlaboratory comparison exercises for the determination of organic compounds. The results from the second interlaboratory study using the interim reference material have been used in conjunction with NIST measurements to assign concentration values for the compounds of interest. This interim reference material is now available to laboratories involved in EPA  $\text{PM}_{2.5}$  research programs for use as a control or reference material. The second  $\text{PM}_{2.5}$  material collected in Baltimore has been distributed to over 20 laboratories as part of the third NIST/EPA intercomparison study, and results will be available in early 2005.

**Impact:** The development of SRMs to support measurements for organic species in fine PM will expand the quality assurance capabilities to important source markers and species critical to human health.

**Future Plans:** We are currently investigating alternative approaches to obtaining sufficient quantities of  $\text{PM}_{2.5}$  for preparation of an SRM including preparation of a fine fraction material from existing PM SRMs and/or other total suspended PM. Additional organic compound classes have been identified by EPA for development of additional solution SRMs including additional sugars, saturated and unsaturated acids, and quinones.

**Program:** Environmental Monitoring Technologies

**Title:** Establishing Measurement Traceability for Gaseous Mercury Emissions Monitoring

**Authors:** G.D. Mitchell and W.D. Dorko

**Abstract:** NIST was tasked with providing traceability for measurements of gas phase elemental mercury ( $\text{Hg}^0$ ) for EPA compliance purposes. The typical manner by which NIST provides traceability for the measurement of gas phase constituents is to certify gas mixtures containing those constituents contained in compressed gas cylinders. One of the Specialty Gas companies has developed a procedure for producing high-pressure mixtures of  $\text{Hg}^0$  in nitrogen contained in aluminum cylinders. NIST was requested by EPA to work with this company and obtained mixtures with differing concentration levels of  $\text{Hg}^0$ . NIST had SRMs of Fly Ash, Orchard Leaves and water that contained certified amounts of mercury, so the experimental plan was to use existing standards to calibrate a system to measure mercury in compressed gas mixtures. A commercial instrument was identified and purchased that could analyze samples containing mercury in any of the three matrices; solid, liquid or gas. The most suitable of the SRMs was the mercury in water, so this was quantitatively diluted to the proper concentration and used to calibrate the analytical instrument that was then used to analyze mixtures of  $\text{Hg}^0$  in nitrogen at nominal concentration levels of  $2 \mu\text{g}/\text{m}^3$ ,  $5 \mu\text{g}/\text{m}^3$  and  $20 \mu\text{g}/\text{m}^3$ .

Another means of providing gas mixtures for instrument calibration purposes is to use a mercury vapor generator. One type of generator functions by passing a metered flow of nitrogen over a heated pool of mercury. The concentration of mercury in the gas stream is calculated by knowing the vapor pressure of  $\text{Hg}^0$  at the thermostated temperature of the mercury pool, and the calibrated flow rate of the nitrogen. One system of this type was also evaluated by NIST by setting the parameters to generate mixtures at the same concentration levels as the cylinder gas mixtures.

**Purpose:** To reduce the health risk posed to people, the Environmental Protection Agency (EPA) has announced that it will regulate emissions of mercury from coal and oil fired power plants. The EPA is focusing its effort on both elemental ( $\text{Hg}^0$ ) and ionic ( $\text{Hg}^{++}$ ) mercury. Although coal-fired power plants are the largest source of mercury emissions to the air in the United States, mercury is also emitted from other sources such as municipal waste combustors, medical incinerators and hazardous waste combustors. Mercury emitted from power plants and other sources is carried by the wind and is eventually deposited onto the land and water. Once it enters the water (lakes, rivers and wet lands) it is converted to methylmercury and can enter the food chain. The EPA came to NIST for assistance in providing traceability in mercury gas standards, which are to be used to calibrate monitoring instruments to measure mercury to verify compliance with EPA emission allowances. . To certify a set of standard gas mixtures of mercury vapor in gas cylinders and to evaluate systems that generate mercury vapor mixtures.

**Major Accomplishments:** NIST worked with a commercial Specialty Gas Vendor to procure three sets of gas mixtures of  $\text{Hg}^0$  in nitrogen. The nominal concentrations of the  $\text{Hg}^0$  in the cylinders are  $2 \mu\text{g}/\text{m}^3$ ,  $5 \mu\text{g}/\text{m}^3$  and  $20 \mu\text{g}/\text{m}^3$ . NIST also purchased a  $\text{Hg}^0$  mixture generator

capable of producing mixtures at the same concentration levels as the cylinders. NIST delivered to the EPA three cylinders of mercury in nitrogen whose concentrations are certified and traceable to the SI (International System of Units). Also, a report was submitted detailing the findings concerning the performance of the mercury gas vapor generator.

The primary analytical instrument used to quantify the amount of mercury is a Nippon Instrument Corporation Model MA-2000 Mercury Analyzer (MA-2), which is equipped with a cold vapor atomic absorption (CVAA) detector. The MA-2 is an analytical system that can measure mercury in discrete liquid or solid samples. A weighed amount of a solid or liquid is put into a ceramic boat that is then placed in a chamber of the analyzer. The way in which vapor samples are supplied to the MA-2 is to pass a measured volume of the gas containing the vapor through an external gold trap to collect the Hg. This gold trap is then placed in the MA-2 instrument boat and this is treated as described above for a solid sample. The traps that were used to trap the Hg<sup>0</sup> from the gas samples, either from the cylinders or the generator, were tested to determine that there was complete collection. The analyzer was calibrated periodically with quantitatively diluted Mercury in Water SRM #1641d and the cylinders analyzed and delivered to EPA.

<u>Cylinder Number</u>	<u>Concentration, <math>\mu\text{g}/\text{m}^3</math></u>
CC-162918	$2.25 \pm 0.08$
CC-162789	$5.99 \pm 0.18$
CC-162881	$22.8 \pm 0.68$

The generator was tested at output concentrations similar to those of the cylinders with the following results.

	<u>Concentration, <math>\mu\text{g}/\text{m}^3</math></u>		
	<u>Hg-20</u>	<u>Hg-05</u>	<u>Hg-02</u>
Generator Setting	20.86	5.13	2.48
<u>Measured on MA-2</u>	21.3	4.97	2.50
Difference: Measured to Set	+ 2.1%	- 3.1%	+ 0.8%

The uncertainties given for the cylinders are the expanded Uncertainties and do not exceed 7% relative, which is within the desired range of the project which was to be less than 10%. The output of the generator was within 5% of set point.

**Impact:** The certified cylinder mixtures are to be used by EPA in their program to audit mercury monitoring sites to determine compliance with regulations. Up till this point they had no way by which to provide quality assurance for the audits. The program also provided data on the performance of a mercury generation device and this data showed that this device is a viable alternate option for calibration and audit of mercury monitors.

**Future Plans:** The cylinders containing the mercury mixtures are to be re-analyzed on a periodic basis to determine whether or not there is any degradation of the Hg<sup>0</sup> concentration. Development work has already begun on a method for studying ionic mercury (Hg<sup>++</sup>) to provide traceability for measurements being made in support of EPA's proposed Regulations.

**Program:** Environmental Monitoring Technologies

**Title:** Method Development and Measurements of Polybrominated Diphenyl Ethers (PBDEs) in Tissue, Serum, and Sediment Standard Reference Materials (SRMs)

**Authors:** H.M. Stapleton, J.M. Keller, M.M. Schantz, and S.A. Wise

**Abstract:** A gas chromatography/mass spectrometry (GC/MS) method has been developed to quantify the flame retardants Polybrominated Diphenyl Ethers (PBDEs) in a variety of existing natural matrix Standard Reference Materials (SRMs). The GC/MS method employs on-column cool injection to compensate for the thermal instability of some of the PBDE compounds. Using this method, the full range of PBDE congeners can be examined in tissue, human serum, and sediment matrices. Measurement of these compounds in these SRMs will be used to assign certified values for the concentrations of individual PBDE congeners.

**Purpose:** PBDEs are flame retardant compounds that are commonly added to many plastics, resins and textiles that are then incorporated into products such as TVs, computers, furniture, and carpets. PBDEs can volatilize or leach out of the products in which they are applied and be transported long distances in the environment, due to their physico-chemical properties. PBDEs are now considered ubiquitous environmental contaminants and much attention has been focused on their transport, uptake, and fate in both humans and the environment. Presently, there is an increased need for measurements of PBDEs in environmental matrices and human serum. SRMs with certified concentrations for individual PBDE congeners are currently unavailable, and they are needed to ensure quality control for these measurements.

**Major Accomplishments:** Ten existing natural matrix SRMs have been analyzed for determination of a suite of 26 PBDE congeners. These SRMs include marine mammal tissue, fish tissue, mussel tissue, human serum, marine sediment and house dust. The GC/MS method, which uses on-column cool injection, has allowed for the measurement of the fully brominated PBDE congener (2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether; BDE 209) using an isotope dilution quantification approach. This congener has often been difficult to measure due to its thermal instability. BDE 209 was observed to be the dominant PBDE congener in the sediment and house dust SRMs, and thus, these SRMs will be useful for laboratories interested in routine measurements for BDE 209.

**Impact:** The development of the GC/MS method and the certification of PBDEs in these SRMs have increased the usefulness of these existing NIST SRMs to laboratories that routinely measure environmental organic contaminants. Legislation in the U.S. is now being considered to reduce the use of PBDEs in consumer products. If this legislation is passed, numerous corporations that produce PBDE-laden products (i.e. Motorola, Dell, Apple) will be affected. These companies have expressed interest in having SRMs to test their products to ensure that they conform to these regulations.

**Future Plans:** Other flame retardants such as hexabromocyclododecane (HBCD) are now being used at higher rates as a replacement for PBDEs in some parts of the world. As such, there is

interest in the measurements of HBCD in environmental samples. Additionally, evidence suggests that PBDEs may be metabolized by some organisms to hydroxylated and methoxylated derivatives. Preliminary evidence already suggests that methoxylated PBDEs (MeOBDEs) are present in the marine mammal blubber and cod liver oil SRMs. Measurements are planned for HBCD and MeOBDEs in these environmental matrix SRMs to provide reference values for these new flame retardant related compounds.

**Program:** Environmental Monitoring Technologies

**Title:** Marine Environmental Specimen Bank Activities

**Authors:** P.R. Becker, R.S. Pugh, M.B. Ellisor, J.R. Kucklick, S.J. Christopher, S.S. Vander Pol, R. Day, J.M. Keller, C. Bryan, H.M. Stapleton, and S.A. Wise

**Abstract:** NIST is expanding its environmental specimen banking activities through the recent development of the Marine Environmental Specimen Bank (Marine ESB) at the Hollings Marine Laboratory, Charleston, SC. Through the Marine ESB, the banking of marine mammal tissues has expanded to include the banking of blood and other kinds of samples collected as part of ongoing marine mammal health studies. In addition, the bank now includes bird specimens collected as part of two Department of Interior bird monitoring programs. Future banking will include tissue specimens from other kinds of marine biota and the development of a genetic cryo-bank for marine research. With the increased interest in newly emerging contaminants, the Marine ESB will be a valuable resource for establishing temporal trends for these compounds in marine ecosystems.

**Purpose:** Environmental specimen banking is the long-term preservation of representative environmental specimens for deferred analysis and evaluation. A systematic well-designed specimen bank program is not only a valuable component of real-time monitoring and basic research, but it also enables investigators to extend their research into the past and provides for future verification of analytical results. Formal environmental specimen banks are recognized internationally as integral parts of long-term environmental monitoring and research. Two national environmental banking systems in the U.S. are the CDC and ATSDR Specimen Packaging, Inventory and Repository (CASPIR™) which cryogenically archives specimens for national public health investigations and NIST's National Biomonitoring Specimen Bank (NBSB) which cryogenically archives specimens for environmental research. Both specimen banks include well developed banking protocols, computerized sample tracking (chain-of-custody) systems, maintenance of many forms of data associated with original specimens, and large investments in state-of-the-art facilities and equipment required to store specimens over relatively long periods of time. Both programs have emphasized cryogenic storage, using ultra-cold (-80 °C) electric freezers and liquid nitrogen vapor storage (-150 °C), security systems, and monitoring of storage conditions 24 hours a day, 365 days a year.

The NBSB was originally established in 1979 by NIST at its Center for Neutron Research in Gaithersburg, MD. In 2002, a NBSB satellite facility was established by NIST at the Hollings Marine Laboratory, Charleston, South Carolina. This facility, the Marine Environmental Specimen Bank (Marine ESB) is devoted to the cryogenic banking of environmental specimens collected as part of ongoing research and monitoring programs conducted by other agencies, such as the National Oceanic and Atmospheric Administration (NOAA) and the U.S. Department of the Interior (DOI), in the marine and coastal environment of the USA.

**Major Accomplishments:** Although the banking of marine specimens has always been a major part of the NBSB (banking of mussels and oysters for NOAA's Mussel Watch Program, sediments and fish tissues for NOAA's National Status and Trends Program, and marine



mammal tissues for NOAA and DOI), the establishment of the Marine ESB at the Hollings Marine Laboratory in association with NOAA, two institutions of higher learning and research, and a State marine research laboratory, has provided major resources and support for expansion of specimen banking nation-wide. The National Marine Mammal Tissue Bank, which was established by Federal legislation in 1992, is maintained by NIST for the National Marine Fisheries Service and the Fish and Wildlife Service as a component of the NBSB and Marine ESB, with the Marine ESB providing the lead. Presently, NIST maintains 2,504 tissue samples collected from 885 individuals representing 37 species of marine mammals from throughout the US coastal waters, including Alaska. These samples are collected from strandings, animals taken incidentally in fishing operations, and animals harvested by Alaska Natives for food. Since the establishment of the Marine ESB, NIST has used its cryogenic banking expertise to develop protocols and to collect and archive blood and blubber samples for NOAA's ongoing bottlenose dolphin health assessment studies, eggs collected as part of a DOI environmental monitoring program on Alaska seabird colonies, and eggs and feathers collected as part of a DOI peregrine falcon monitoring program. To date, blood and blubber have been collected from 215 bottlenose dolphins, 434 eggs have been archived from five species of arctic seabirds throughout Alaska as well as 9 eggs and 26 feathers from the peregrine falcon program.

The primary function of the Marine ESB is to provide samples for retrospective analysis. In 2004, aliquots of blubber specimens collected from California sea lions during 1993 to 2002 and banked in the NMMTB were analyzed by NIST for polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), which are synthetic anthropogenic flame retardants that have now become ubiquitous contaminants and temporal trends have indicated concentrations are increasing rapidly in many matrices. The analysis of these banked samples was to determine if temporal trends for these compounds are also discernable in this species of marine mammal that is common on the west coast of the United States. The results indicate a significant temporal trend with HBCD with a doubling time of 2 years. The specimens archived in the Marine ESB will provide a valuable resource for investigating temporal environmental trends in these new compounds and for determining patterns of past exposure in marine biota.

**Impact:** The establishment of the Marine ESB in association with the Hollings Marine Laboratory has provided a renewed interest in specimen banking as part of marine environmental monitoring and research. Additional kinds of specimen have been added to the bank and additional sponsors have contributed to the expansion of the banking program. With the recognition that newly emerging compounds are appearing in the environment with potential environmental and health effects, the value of the specimens presently held by the bank for determining past exposure patterns and for evaluating temporal trends in concentrations of these compounds is becoming more apparent.

**Future Plans:** NIST will continue to work with the Hollings Marine Laboratory partners and other Federal agencies and partners to expand environmental specimen banking. NIST staff are presently working with these partners to add banking as part of a future sea turtle health assessment program, to reinstitute banking as part of the Mussel Watch Program, to establish a genetic cryo-bank as part of a National Genetics Archive initiative for marine biota, and to expand the banking of bird specimens to include other kinds of species and types of tissue samples on a national and international level. And finally, existing specimens being held by the bank are

being identified for future work on identifying and measuring new contaminants of interest as related to issues on ocean and human health.

**Program:** Environmental Monitoring Technologies

**Title:** Standard Reference Materials (SRMs) for Contaminants in Marine Tissue and Sediment

**Authors:** S.J. Christopher, R.D. Day, W.C. Davis, S.E. Long, R.S. Pugh, M.M. Schantz, J.R. Kucklick, D.L. Poster, J.M. Keller, H.M. Stapleton, K.S. Sharpless, C. Phinney, B. J. Porter, E.A. Mackey, R.O. Spatz, C.E. Bryan, J.R. Sieber, R. Zeisler, S.A. Wise, and G.C. Turk

**Abstract:** New classes of organic and organometallic contaminants have been measured in various marine tissue and sediment SRMs and in SRM 1947 Lake Michigan Fish Tissue. New analytical approaches have been developed to certify trace elements in SRM 1947 and SRM 2703 Marine Sediment for Microsampling.

**Purpose:** Targeted environmental monitoring efforts, regulatory pressures and compounds of emerging concern are expanding the list of potentially toxic contaminants that impact marine systems and challenging the analytical community to develop new measurement technologies for organic pollutants and trace metals. NIST is responding by providing marine matrix SRMs to the marine environmental research community for method validation and quality assurance purposes and is at the forefront of developing and disseminating new analytical technologies for measuring contaminants in marine reference materials.

**Major Accomplishments:** The value assignment of SRM 1947 Lake Michigan Fish Tissue highlights the collaborative effort undertaken to provide a marine reference material with a comprehensive suite of contaminant values, as well as information on nutritive properties. Several classes of compounds are represented in this material, ranging from selected trace elements, including total mercury and methylmercury, and organic contaminants, including polychlorinated biphenyl (PCB) congeners, chlorinated pesticides, and polybrominated diphenyl ether (PBDE) congeners to proximates and fatty acids. New methods were developed to measure compounds like PBDEs, which are flame retardant compounds added to consumer plastic products. These compounds are chemically similar to PCBs, with levels increasing in the U.S. population. PBDEs are currently being measured in two marine sediment SRMs (1941b Organics in Marine Sediment and 1944 NY/NJ Waterway Sediment) and three Mussel tissue SRMs (1974b, 2977 and 2978). All PBDE measurements required the preparation of custom primary standards from chemically pure solutions and solids, reduction of background levels in the analytical blank and development of gas chromatography mass spectrometry (GC/MS) methods to accommodate these thermally labile compounds.

Significant effort went into development of new complementary strategies for determination of organometallic species in marine tissue SRMs. For example, microwave assisted acid extraction was used in combination with solid phase microextraction gas chromatography-inductively coupled plasma mass spectrometry (SPME-GC-ICPMS) to measure organic and inorganic fractions of Hg and organotin compounds in SRMs 1947, 1946 (Lake Superior Fish Tissue), and bivalve tissues, SRM 1566b Oyster Tissue, SRM 2976 Mussel Tissue (Trace Elements and Methylmercury) and SRM 2977 Organics in Mussel Tissue. Some of these SRMs were also

screened for As and Se content using liquid chromatography coupled to collision cell ICPMS, with the goal being to eventually provide concentration values to SRM customers tasked with measuring speciated forms of metals in various environmental matrices.

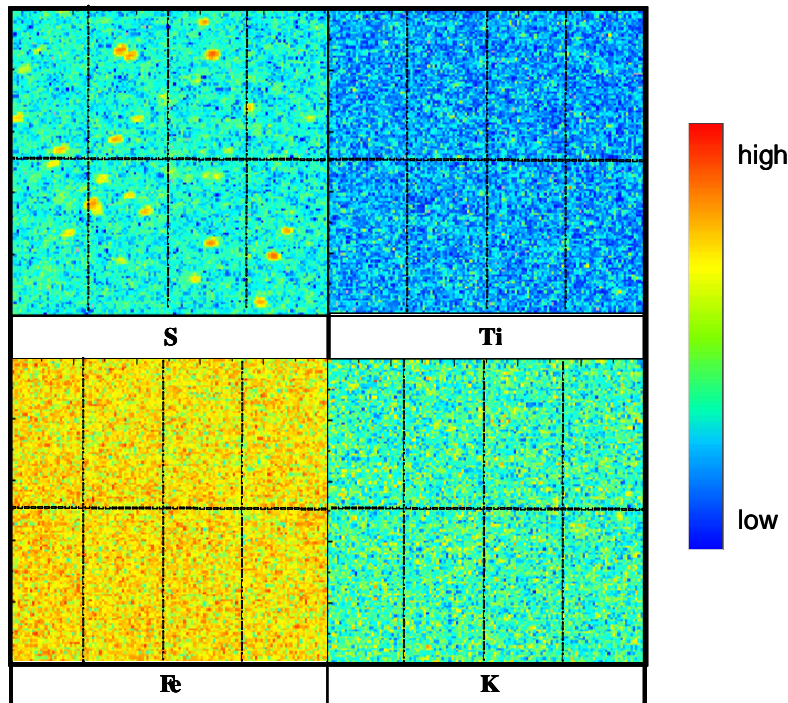
A new certification strategy was tested and implemented for certification of trace elements in SRM 1947 that is applicable to all homogeneous reference materials. Where multiple jars of a homogeneous NIST SRM need to be analyzed, a new standard additions/internal standard procedure was created to streamline certification measurement efforts. In the new procedure, multiple (typically 6) samples of the candidate CRM are accurately weighed into digestion vessels and gravimetrically spiked with an internal standard solution. Increasing amounts of a multi-element spike solution are then gravimetrically added to each vessel, ranging from no spike to a high spike, to effect a standard additions calibration curve. From this point on all measurements of the digested samples will be based on analyte/internal standard ratios, and all sample handling, including removal of the solutions from the digestion vessels and any subsequent dilutions, does not need to be done quantitatively. This is one of the main benefits of this approach. The other benefit is that we do not have to perform sample splits on each sample (SRM jar) to be measured. Values and uncertainties are calculated by linear regression of the measured analyte/internal standard ratios vs. the amount of standard added, and the slope of the standard additions curve can be used to predict concentration values in similar matrix controls run concurrently during experiments.

SRM 2703 is a marine sediment collected at the mouth of the Baltimore Harbor, primarily intended for use in evaluating analytical methods for the direct determination of selected elements in solid samples of marine or fresh water sediment and similar matrices. SRM 2703 was specifically developed for microsampling techniques. Direct and slurry sampling, as well as dissolution techniques using typically milligram size samples can employ this SRM to benchmark their procedures. A thorough homogeneity assessment of the material was conducted using instrumental neutron activation analysis (INAA), and laser ablation inductively coupled mass spectrometry (LA-ICPMS), micro-beam X-ray fluorescence ( $\mu$ XRF) and micro proton beam induced X-ray emission ( $\mu$ PIXE, see Fig. 1) techniques complemented the INAA assay with homogeneity results for significantly smaller sample sizes. Additional measurements with several solid sampling procedures and dissolution procedures were provided by collaborating laboratories with the following techniques: atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICPAES) and ICPMS, and X-ray fluorescence (XRF). All assays were designed to establish communicability of values between those conventionally certified in SRM 2702, representing the parent material, and the SRM 2703 measured at small sample sizes. These measurements confirmed that the composition of the material had not changed in processing and that the measured values in SRM 2702 can be utilized for value assignment of SRM 2703.

**Impact:** Study of complex marine environmental systems requires wide ranging chemical measurements performed in many laboratories over long periods of time. Meaningful knowledge can only be extracted from such studies if the quality of these chemical measurements is high. The program examples highlighted here show that CSTL's collaborative measurement capabilities lead to innovative reference materials and measurement technologies aimed at improving and assuring chemical measurement quality.

**Future Plans:** Work will be dedicated to developing analytical methods and measuring environmental compounds of emerging concern in current issue and future marine tissue and sediment SRMs, including, perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), other types of brominated flame retardants, classes of compounds like phthalate esters and their metabolites, which are prevalent in plasticizers, and representative compounds comprising the range of pharmaceutical and personal care products. We will also measure methylmercury and organotin compounds in marine sediment and tissue SRMs.

Figure 1. Micro-PIXE images of the SRM 2703 bottle #1291 sample by I. Bogdanović Radović, Ž. Pastuović, and M. Jakšić, Rudjer Boskovic Institute, Zagreb, Croatia. Samples were analyzed using a 3 MeV focused proton beam. Micro-PIXE images were collected for all elements found in the PIXE spectrum. The total scan size of  $750\text{ }\mu\text{m} \times 750\text{ }\mu\text{m}$  was divided in 8 equal regions, each being quantitatively evaluated. Only sulfur showed heterogeneity directly observable from the 2D maps in all SRM 2703 samples. Detailed analysis of the spectra from each of the 8 smaller regions revealed homogeneity of SRM 2703 for Al, Si, Cl, K, Ti, Mn, and Fe at the probed  $1\text{ }\mu\text{g}$  to  $7\text{ }\mu\text{g}$  sample size



**Program:** Environmental Monitoring Technologies

**Title:** Standards Development and Measurements to Support Global Climate Change

**Author:** G.C. Rhoderick

**Abstract:** Several species of gases found in the atmosphere that can contribute change to the radiative environment of the earth have been developed as gaseous primary standards (PSMs). These gases are considered greenhouse gases and have been monitored throughout the atmospheric environment community worldwide for many years. These gases have also gained increased importance since the Kyoto protocol was designed and implemented to promote reduced emissions of greenhouse gases. PSMs were developed previously for methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), tetrafluoromethane (CF<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), and sulfur hexafluoride (SF<sub>6</sub>).

This past year an additional compound, 1,1,1,2-tetrafluoroethane (Halocarbon 134a), was studied and standards developed for the State of California Air Resources Board (CARB). This compound is a replacement for halocarbons previously used as refrigerants but being phased out due to their high warming potential. Additionally, new PSMs were prepared at atmospheric levels and added to a suite of previously prepared standards. These compounds include carbon tetrachloride, chloroform, trichlorotrifluoroethane (CFC-113), 1,1,1-trichloroethane and trichloroethylene. NIST primary standards (PSMs) for global climate change measurements have served three purposes this past year. Firstly, CARB needed NIST traceable standards of 1,1,1,2-tetrafluoroethane for their ambient and automobile measurement programs. Secondly, our laboratory participated in three comparison studies for PSMs. One study, CCQM-P41 Greenhouse Gases, involves several national metrology institutes (NMIs) and laboratories from the World Meteorological Organization (WMO) in an effort to evaluate and improve the preparation and measurement capability of gravimetrically prepared methane and carbon dioxide mixtures. A second separate study in collaboration with NOAA/CMDL compared methane PSMs. The third was also an international comparison, CCQM-K15, for CF<sub>4</sub> and SF<sub>6</sub>.

**Purpose:** PSMs were developed to support the in-house standards base for SRM certification, international intercomparison programs between national NMIs to determine equivalence, the NIST FTIR spectral database project and the International Halocarbon Experiment (IHALACE) program sponsored by the WMO, NOAA and NASA.

**Major Accomplishments:** A total of 22 gravimetrically prepared CH<sub>4</sub> in air primary standards, now exist and are used to define the NIST primary calibration methane scale for laboratory measurements and traceability. The entire suite of primary standards range in concentrations from 0.8 μmol/mol to 10 μmol/mol. Eight of these PSMs also contain nitrous oxide, dichlorodifluoromethane and trichlorofluoromethane. Two PSMs were submitted by NIST for evaluation in the CCQM-P41 Greenhouse Gas comparison study. One PSM contains methane in air and the second mixture contains carbon dioxide in air. Three PSMs containing methane in air were also compared to methane in air PSMs prepared at the Climate and Diagnostics Laboratory at NOAA. A suite of three standards containing CF<sub>4</sub> and SF<sub>6</sub> were prepared to value assign the CCQM-K15 sample. A suite of four standards containing carbon tetrachloride, 1,1,1-

trichloroethane, chloroform, trichlorotrifluoroethane and trichloroethylene in air and five standards prepared in nitrogen containing the same compounds now exist at NIST. This suite of primary standards range in concentrations from 5 pmol/mol (ppt) to 100 pmol/mol. The PSMs containing these halogenated species can now be used to analyze real air samples as part of the IHALACE program.

**Impact:** Development of these PSMs will underpin the SRM program and serve to establish equivalency between national NMIs and atmospheric research measurement laboratories.

**Future Plans:** In 2005, these new PSMs containing halogenated species will be used to analyze and determine concentrations in unknown real air samples from remote sensing sites as part of the IHALACE program; an international comparison between research laboratories that make real air measurements and/or prepare them on PSMs. Also, it is anticipated that PSMs will be developed for many species that contribute to global warming. These PSMs will lay the foundation for which atmospheric measurements can be underpinned and possible development of new SRMs to support national ambient monitoring measurements of those species.

**Program:** Environmental Monitoring Technologies

**Title:** Influence of Oxygen on the Shelf Life of Coal Standard Reference Materials (SRMs)

**Authors:** R. Zeisler and W.D. James (TAMU)

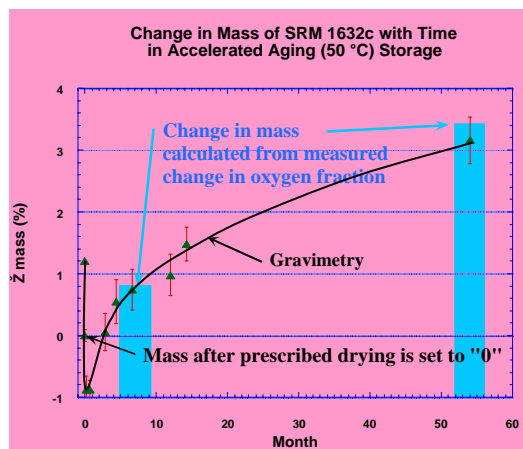
**Abstract:** Long-term stability of SRMs is essential to customers' use of the materials. CSTL scientists and collaborators validated the stability of coal SRMs under proper storage conditions. Oxidative environments in combination with elevated temperatures have been found to promote the oxidation of coal samples and lead to changes in composition.

**Purpose:** Based on reports by users of the previously (1985) issued SRM<sup>®</sup> 1632b Trace Elements in Coal of a change in the measured values of the carbon mass fraction, the new values being about 1.6% lower than previously measured, investigations to validate the long-term stability of coal samples were initiated. A definition of the chemistry of the changes was desired.

**Major Accomplishments:** Initial evidence of change was provided by trace element data in the SRM 1632b material, which indicated approximately a change in mass fraction values similar to the reported carbon change for a number of elements determined by INAA. While a change in carbon content through loss of CO<sub>2</sub> may have been a plausible explanation for lower than previously measured carbon values, the measured decrease of a larger number of elemental content values may be explained in a gain of matrix mass, such as by irreversible oxidation and therefore increased matrix mass.

The newly developed SRM 1632c Trace Elements in Coal (Bituminous) was selected for the study. Twenty-six samples each were stored at three conditions: in liquid nitrogen vapor and at room temperature in the original containers packaged under argon, and for accelerated aging at 50 °C open to air. Under proper storage, the samples showed stable mass during the more than 4-year observation; only the ones stored open at higher temperature gained weight. To directly measure the presumed oxidation, a fast (14-MeV) neutron activation analysis (NAA) procedure was employed to determine mass fractions of oxygen in the coal samples.

The 14-MeV NAA is an effective procedure for the direct determination of oxygen. It demonstrated sufficient precision and accuracy to determine a relative change of about 5 % or more, in the oxygen mass fraction of about 11 %. To evaluate the sample stability, test points were set at 6 and 54 months for the oxygen determination, more frequent gravimetric tests were carried out for the samples in the open 50 °C storage. The gain in mass and in oxygen for the latter samples is illustrated in the figure. All gain in mass can be explained by the gain in oxygen content. No change in oxygen content was measured in the other storage





conditions. As further validation of this gain in sample mass of coal under oxidative storage, an analytical comparison of trace element content in the three storage conditions showed a lowering in mass fraction for 22 trace elements corresponding to the gain in sample mass.

**Impact:** The measurements give assurance that properly packaged coal SRMs, protected from oxygen and heat, are stable during their shelf life. Gravimetric monitoring of coal SRMs during shelf storage should be employed by NIST and customers alike as a cost-effective quality measure.

**Program:** Environmental Monitoring Technologies

**Title:** Studying the Chemistry of Pharmaceuticals in Wastewater  
*Exploratory Research Project*

**Authors:** M. Bedner and W.A. MacCrehan

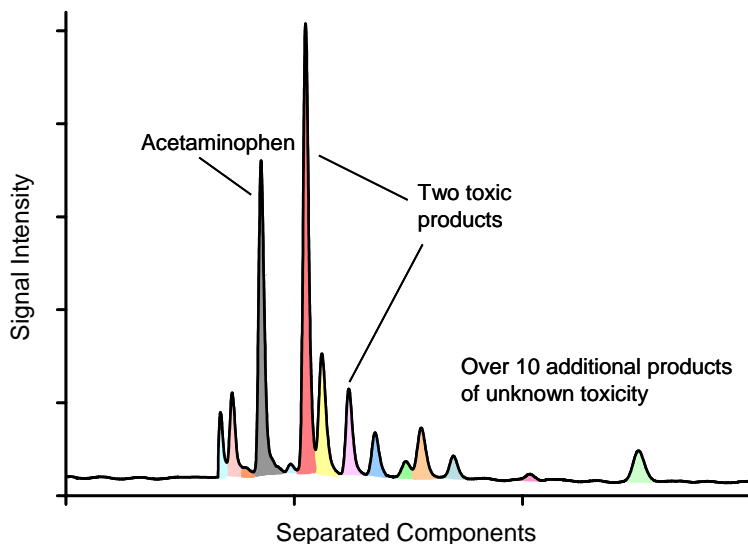
**Vision:** To establish the NIST role in the measurement of environmentally-important pharmaceutical compounds.

**Purpose:** Pharmaceuticals and personal care products (PPCPs) are increasingly being recognized as a threat to human health and the environment. PPCPS are continuously released into the environment from human and agricultural waste and are frequently subject to waste treatment processes. Chlorination is the most widely-used chemical process for disinfecting wastewater and drinking water. Chlorine is a strong, non-selective oxidant that is capable of rapidly transforming pharmaceutical compounds. Understanding the chemical and toxicological nature of the transformation products is an important first step to determining what compounds should be measured in the environment.

**Context:** This research represents a new focus area in CSTL and was awarded exploratory research funds in FY04.

**Scientific and technical research and development:** This project was made possible by the new LC/MS system in our laboratory. The identification of unknown transformation products using mass spectrometric detection is critical in investigating this measurement problem.

**Major Accomplishments:** Four pharmaceutical compounds that are frequently detected in the environment were evaluated and included acetaminophen, metoprolol, sulfamethoxazole, and diclofenac. We have begun investigations of the pharmaceutical transformations using calibrated doses of chlorine (added as hypochlorite). Liquid chromatography was used to separate reaction products, which were evaluated and identified using four detection modes. All compounds were significantly transformed by reaction with chlorine. Acetaminophen was shown to form two toxic products, benzoquinone and *N*-acetyl-*p*-benzoquinoneimine, and at least ten additional products (see chromatogram). Metoprolol reacted to form one major product, a chloramine. Sulfamethoxazole formed two major products, both of which have a chlorine atom in the molecule, but only one of which appears to be a chloramine. Diclofenac forms at least five products, one of which has an additional chlorine atom. For all



compounds, the products of the reactions tended to be more hydrophobic than the parent pharmaceutical, which might make them more bioaccumulative.

**Impact:** These preliminary investigations have revealed potential target compounds for measurement in the environment. This critical information will be used by environmental researchers determining the importance and fate of pharmaceutical compounds.

**Future Plans:** This project is still in its early stages, so there are many important aspects that need to be addressed. The transformation rates of the pharmaceutical compounds need to be evaluated at the ppb levels typically found in wastewater to verify that the reactions will be significant. Also, as products are identified, targets for measurement in the environment need to be determined based on the potential for toxicity and/or bioactivity. In addition, there are other chemical processes including chloramination, dechlorination, and ozone-disinfection that might transform pharmaceutical compounds. The effects of these water treatment processes on pharmaceuticals will be investigated.

**Program:** Environmental Monitoring Technologies

**Title:** NIST Aids NOAA with Bottlenose Dolphin Health Assessments

**Authors:** J.R. Kucklick, S.J. Christopher, P.R. Becker, R.S. Pugh, M. Ellisor, J.M. Keller, C.E. Bryan, and J.E. Yordy

**Abstract:** NIST aids the National Oceanographic and Atmospheric Administration (NOAA) in their long-term bottlenose dolphin health assessments through developing and implementing a protocol for samples collected for persistent organic pollutant and trace element analysis. NIST also provides measurements of persistent organic pollutants and trace elements in dolphin samples, ensuring continuity for the project and high accuracy results. To date, the NIST protocol has been used in 11 dolphin health assessments and will be used in seven assessments planned for fiscal year 2005. The data and expertise provided by NIST are vital in interpreting toxicological and health-related information collected on the animals.

**Purpose:** Since 2000 NOAA has studied the health of bottlenose dolphins by collecting data and samples from animals captured and then released at locations along the US Atlantic and Gulf Coasts. Bottlenose dolphins accumulate persistent organic pollutants, such as polychlorinated biphenyls (PCBs) and brominated flame retardants to some of the highest observed levels in wildlife, hence they are at risk from the toxic effects of these compounds. For instance, in Sarasota Bay, where sampling occurs twice per year, there is nearly complete mortality of dolphin calves born to first-time mothers. It is hypothesized that persistent organic pollutants offloaded from the mother via milk play a major role in this reproductive failure. In 2002 NOAA asked NIST to provide technical assistance for the project by (1) designing a protocol for collecting, handling, and storing blood, blubber, and skin to be used for organic contaminant and/or trace element analyses (2) permanently archiving blood and blubber samples for future study, (3) analyzing persistent organic pollutants and trace elements in samples collected during dolphin health assessments, and (4) providing technical assistance in the field during sample collection. The collaboration between NIST and NOAA on this project emerged from the recognition by NOAA that NIST is a leader in the field of environmental specimen banking, quality assurance, and environmental analysis. Data supplied by NIST will provide basic understanding of contaminant burdens in bottlenose dolphins and provide exposure data for toxicological studies performed on the animals.

**Major Accomplishments:** NIST developed a detailed protocol for collecting samples from bottlenose dolphins during health assessments. The protocol covers the collection of skin, plasma, whole blood, and blubber samples to be analyzed for trace elements (including mercury), persistent organic pollutants, and perfluorinated compounds, such as perfluorooctane sulfonate (PFOS). Since 2002 NIST personnel have successfully applied the collection protocol during 11 health assessments from four locations resulting in samples from over 150 dolphins. Seven additional health assessments are scheduled for fiscal year 2005. Subsamples of plasma and blubber are being archived in the Marine Environmental Specimen Bank. Blubber and blood samples are being analyzed for over 100 individual persistent organic pollutants including brominated flame retardants. Blubber samples from 22 mother-calf pairs were analyzed revealing that the majority of the persistent organic pollutant load is passed to the calf. Milk

samples collected from the mother dolphins and blood from mother and calf dolphins are currently being examined to better understand contaminant transfer from milk, especially for the brominated flame retardant compounds. Trace elements including mercury were determined in blood samples from dolphins sampled in Sarasota Bay, Florida and coastal New Jersey. A technique has also been developed to measure mercury in skin biopsy samples. This may allow the use of skin collected from remote dart biopsies to be used for the assessment of mercury.

**Impact:** A number of different research groups are involved in bottlenose dolphin health assessments. The protocol established by NIST provides for a common procedure for all projects collecting samples for persistent organic pollutant or trace element analysis. Samples collected by NIST for NOAA are archived in the Marine Environmental Specimen Bank—a facility constructed specifically for the storage of environmental samples in a controlled, non-contaminating environment. Analytical work completed for NOAA ties measurements to a national metrology laboratory with a history of providing high-quality measurement data to NOAA. Since the dolphin health assessments are long-term projects, NIST's involvement will provide continuity in the analytical data generated on the project.

**Future Plans:** NIST will continue to work with NOAA as they expand their dolphin health assessment project to other areas along the coastal US. Work is underway to make use of high throughput techniques for the analysis for persistent organic pollutants in blood and blubber. The target list will be expanded to include other types of compounds of emerging concern, such as additional flame retardants and perfluorinated compounds. A control material for dolphin blood will be developed and value assigned to provide a benchmark for blood analysis.

**Program:** Environmental Monitoring Technologies

**Title:** New Standard Reference Material (SRM) for Organic Contaminants in House Dust

**Authors:** M.M. Schantz, J.M. Keller, J.R. Kucklick, D.L. Poster, H.M. Stapleton, S. Vander Pol, and S.A. Wise

**Abstract:** House dust is a repository of pesticides and other chemicals used indoors or tracked in from outdoors. NIST has produced two Standard Reference Materials (SRM 2583 and SRM 2584) for lead and other trace elements in a house dust matrix. SRM 2585, Organic Contaminants in House Dust, will be issued with concentration values assigned for pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and polybrominated diphenyl ether (PBDE) congeners.

**Purpose:** House dust was collected and analyzed in survey studies, such as the National Health Exposure Assessment Study (NHEXAS), as one indicator of indoor exposure. Pesticides associate with house dust primarily through interior use of pest control formulations, vapor intrusion from foundation and crawl space treatments, and tracking-in of lawn and garden chemicals. PAHs derive from indoor sources such as combustion, cooking, and smoking, and from track-in of contaminated yard soil or residues from garage floors. PBDEs are commonly used flame retardant compounds added to many plastics, resins and textiles which are then incorporated into products including TVs, computers, furniture and carpets. A house dust reference material with values assigned for a wide range of organic contaminants is needed for quality control in these measurements.

**Major Accomplishments:** Over 100 contaminants, including pesticides, PAHs, PCB congeners, and PBDE congeners, will be value assigned in SRM 2585 using an approach similar to that used for other natural matrix reference materials, such as mussel tissue<sup>1</sup> and sediment<sup>2</sup>. Three methods were used to quantify a number of pesticides, PAHs, and PCB congeners in the house dust. Using one of the methods, the material was found to be homogenous at a 1 g sample size. *Cis*- and *trans*-chlordane are present in the material at concentrations between 150 µg/kg and 250 µg/kg. Fluoranthene and pyrene are present in the material at concentrations between 3000 µg/kg and 4500 µg/kg. The individual PCB congeners are lower in concentration (<50 µg/kg for each congener). Two methods were used to value assign the PBDE congeners in SRM 2585. PBDE 209 was the dominant PBDE congener in SRM 2585 at a concentration of 2600 µg/kg.

**Impact:** The house dust SRM 2585 will provide a control sample for laboratories routinely monitoring indoor dust. With the increased interest in the PBDE concentrations in all types of environmental samples, the assignment of concentrations for this group of compounds in many different matrices, particularly those associated with human exposure, will be important.

**Future Plans:** As methods are developed for additional groups of chemicals important in human exposure studies, the house dust SRM will be analyzed for these compounds to expand its utility.

1. Poster, D.L., Schantz, M.M., Kucklick, J.R., Lopez de Alda, M., Porter, B.J., Pugh, R., and Wise, S.A., "Three New Mussel Tissue Standard Reference Materials (SRMs) for the Determination of Organic Contaminants," *Anal. Bioanal. Chem.*, 378, 1213-1231 (2004).
2. Wise, S.A., Poster, D.L., Schantz, M.M., Kucklick, J.R., Sander, L.C., Lopez de Alda, M., Schubert, P., Parris, R.M., and Porter, B.J. "Two New Marine Sediment Standard Reference Materials (SRMs) for the Determination of Organic Contaminants," *Anal. Bioanal. Chem.* 378, 1251-1264 (2004).

**Program:** Environmental Monitoring Technologies

**Title:** Interlaboratory Comparison Exercises for Organic Contaminants and Trace Elements in Marine Mammal Tissues

**Authors:** J.R. Kucklick, S.J. Christopher, P.R. Becker, R.S. Pugh, M.B. Ellisor, S.S. Vander Pol, E.A. Mackey, R.O. Spatz, B.J. Porter, M.M. Schantz, G.C. Turk, and S.A. Wise

**Abstract:** The National Institute of Standards and Technology (NIST), in support of the National Oceanic and Atmospheric Administration's Marine Mammal Health and Stranding Response Program (NOAA/MMHSRP), conducts annual interlaboratory comparison exercises for the determination of chlorinated pesticides, polychlorinated biphenyl congeners, and trace elements in marine mammal tissues. The exercises provide one mechanism for laboratories to evaluate their measurement quality and comparability for these constituents in marine mammal tissues. In the 2003 exercise, a total of 49 laboratories participated in the organic contaminant and trace element exercises including laboratories from nine countries in addition to the U.S. Participants were requested to analyze a control material and an unknown sample for a variety of constituents. Cumulative results compiled from exercises conducted from 1999 to 2003 indicate that laboratory agreement with target exercise values improves with the number of years a laboratory participates in the exercise.

**Purpose:** Laboratories measuring contaminants in the marine environment must assess the accuracy and precision of their measurements. Quality control of measurements made on marine environmental samples is vital to the accurate assessment of marine pollution and its effects on wildlife and human health. Representative control materials needed to benchmark analytical methods and measurements are often limited or not available for many marine matrices of interest (*e.g.*, marine mammal tissues and marine fishes). Consequently, analysis may be undertaken on samples without control materials that are similar in nature to the sample. To help address this need, the National Institute of Standards and Technology's (NIST) Analytical Chemistry Division, with the help of other U.S. Government sponsors, initiated several programs to assess the data quality of laboratories performing chemical measurements on marine-related samples.

NIST helps benchmark and improve the quality of analytical data on the marine environment by conducting interlaboratory comparison exercise programs. The first such program for environmental measurements was initiated in 1987 and funded in part until 2000 by the National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends Marine Monitoring Program (NOAA/NS&T). This program provides mechanisms for assessing the interlaboratory and temporal measurement comparability of polycyclic aromatic hydrocarbons, polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides in bivalve mollusk, sediment, and fish samples. The program includes components for developing improved analytical methods, producing NIST Standard Reference Materials (SRMs) and other control materials, conducting annual interlaboratory comparison exercises, and coordinating workshops to discuss exercise results. This program continues as the NIST Intercomparison Program for Organic Contaminants in the Marine Environment with partial support from fees paid by the



participants, and it served as the model for the Interlaboratory Comparison Exercises Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues.

**Major Accomplishments:** NIST expanded the Interlaboratory Comparison Exercise for Organics in Marine Mammal Tissues in 1999; and the trace element complement to the exercise was formalized in 2000. Since this time the participation has increased dramatically. For example, the number of laboratories participating in the organic exercise increased from 10 in 1999 to 25 in 2003. The exercises are highly international with nine countries involved in the trace element exercise and six in the organic exercise in 2003. Results from the program led to the development of a suite of control materials for trace elements in marine mammal tissues and the production of one Standard Reference Material, SRM 1945 Organics in Whale Blubber. The organics exercise has been successful as a source of data on new constituents in SRM 1945. For example, fatty acids and brominated flame retardants were determined in the unknown and in SRM 1945 by five and six laboratories, respectively. The trace element exercise has led to the development of three trace element control materials from marine mammal livers, a pilot whale liver homogenate in 1991, and beluga whale and pygmy sperm whale liver homogenates in 1997 and 2003, respectively. Independent analytical methods at NIST (inductively coupled plasma mass spectrometry and instrumental neutron activation analysis) produced data to provide a reliable benchmark to assess the performance of participating laboratories. The trace element exercise also used an innovative approach to arrive at a consensus mean and uncertainty data using a maximum likelihood solution model developed by Rukhin and Vangel at NIST.

**Impact:** Comparability of measurements for organic contaminants has improved for those laboratories with a longer history of participation in the exercises, e.g., those that have participated since 1999 have improved their accuracy by 10% and their precision by 20%. The SRMs and control materials developed through this program and the interlaboratory comparison exercises are mandated for use by researchers in the U.S. who are funded by NOAA to perform measurements of trace elements and organic contaminants in marine mammal tissues.

**Future Plans:** NIST will continue to administer and coordinate interlaboratory comparison exercises for chemical analysis of marine mammal tissues. Future exercises will ask participants for compounds of emerging interest such as brominated and fluorinated compounds, toxaphene congeners, and organometal contaminants, such as butyl tins and methyl mercury. The next round of interlaboratory comparisons will occur in 2005. Also in 2005, the data compiled from the exercises using SRM 1945 as a control will be used to assist in updating the Certificate of Analysis with values for additional polychlorinated biphenyl congeners, brominated diphenyl ether congeners, toxaphene, and fatty acids.

**Program:** Environmental Monitoring Technologies

**Title:** Simultaneous Determination of Sulfur Isotopic Composition and Concentration in Environmental Samples Using a  $^{33}\text{S}/^{36}\text{S}$  Double Spike Technique

**Authors:** J.L. Mann, W.R. Kelly, and R.D. Vocke

**Abstract:** A new analytical technique that is both highly accurate and precise has been developed for the simultaneous determination of sulfur isotope composition and concentration of low concentration samples. The technique combines multi-collector thermal ionization mass spectrometry (TIMS) with a  $^{33}\text{S}/^{36}\text{S}$  internal standard and has been applied to three international sulfur standards (IAEA-S-1, IAEA-S-2, and IAEA-S-3) from the International Atomic Energy Agency (IAEA). The  $\delta^{34}\text{S}$  values determined were  $-0.32\text{‰} \pm 0.04 \text{‰}$  (1s),  $22.65 \text{‰} \pm 0.04 \text{‰}$  (1s), and  $-32.47 \text{‰} \pm 0.07 \text{‰}$  (1s) for IAEA-S-1, IAEA-S-2, and IAEA-S-3, respectively. The uncertainties reported for sulfur isotopic composition are comparable to or better than those obtained by isotope ratio mass spectrometry (IRMS). The precisions on the concentration measurements are typically 0.1 % or better for sample sizes of approximately 15  $\mu\text{g}$  to 65  $\mu\text{g}$ .

**Background:** Recently the National Resource Council (NRC) identified several “Grand Challenges” in environmental research for the next generation. Included in these is “understanding Earth’s major biogeochemical cycles and their interaction with the global climate”.

The in the atmosphere and the particles has important Sulfate aerosols interact outgoing terrestrial radiation and indirectly function as that influence concentration surface reflectivity, and the (IPCC, 1995). The majority derived from gas-to-particle emissions result in



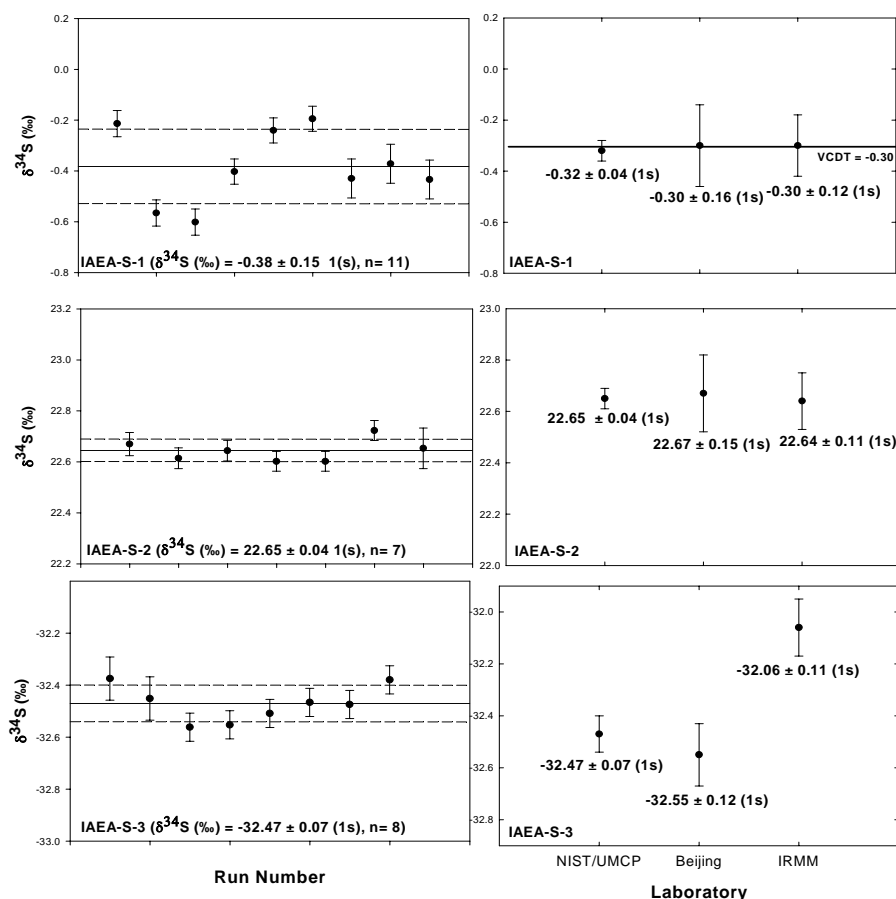
biogeochemical cycling of sulfur formation of sulfate aerosol consequences for global climate. directly with incoming solar and through scattering and absorption cloud condensation nuclei (CCN) and size of cloud droplets, droplet radiative properties of clouds of sulfate aerosol particles conversion of anthropogenic  $\text{SO}_2$  submicron secondary aerosols.

These submicron aerosols, with a residence time in the atmosphere of a few days to a week, are able to influence atmospheric composition both downwind of industrialized areas and in remote areas of the world. In the 1990s researchers recognized the need to determine the origin of submicron sulfate aerosols in order to assess the impact of increasing anthropogenic sulfur emissions on the natural atmospheric sulfur cycle and global climate. Assessing the global influence of anthropogenic activity in the northern hemisphere on the climate is becoming increasingly more important with the growing population and commensurate use of fossil energy.

**Purpose:** The variability of sulfur isotope ratios in nature, caused by mass-dependent fractionation during biogeochemical processing, provides a chemical tool for tracing the various sources of sulfur aerosols and a useful tool for understanding the sulfur cycle. Snow and ice cores provide archives of the sources, sinks, and processing of sulfur that reflect changes in this cycle through time. These archives can be used to assess the current and historical changes in

sulfur source contributions to remote regions of the Earth including polar, temperate, and tropical regions. Typical concentrations of sulfate in these regions are 25 to 100 ng/g (ppb); thus, 300 g to 4000 g of sample is required to obtain enough sample ( $\sim 33 \mu\text{g S}$ ) for traditional isotope ratio mass spectrometric (IRMS) analysis. Global atmospheric sulfur cycling is a dynamic process that varies on short timescales and these large quantities of sample can mask seasonal changes in sulfur sources. Consequently, an analytical technique that allows the reduction of sample needed for analysis is required to minimize masking and increase the resolution.

**Technical Background:** In this study we have focused on the use of multi-collector TIMS combined with a  $^{33}\text{S}/^{36}\text{S}$  internal standard for simultaneous determination of sulfur **isotope composition**  $\delta^{34}\text{S}$  ( $\delta^{34}\text{S} (\text{‰}) = [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{34}\text{S}/{}^{32}\text{S})_{\text{standard}} - 1] \times 1000$ ) and **concentration** of small ( $< 1 \mu\text{g}$ ) sulfate ( $\text{SO}_4^{2-}$ ) samples. The fundamental limitation to accurate and precise isotopic ratio measurements by thermal ionization is that the measured ratio differs from the true ratio in the source as a result of instrumental fractionation during vaporization of the sample from the filament. To address this changing ratio and to improve precision and accuracy in the  $^{34}\text{S}/^{32}\text{S}$ , a well-characterized  $^{33}\text{S}/^{36}\text{S}$  internal standard was added to the samples and was used to calculate a fractionation factor ( $\alpha$ ) that corrects for this changing ratio (instrumental fractionation) to give the true ratio in the source. The  $^{32}\text{S}/^{33}\text{S}$  ratio that has also been corrected for instrumental fractionation was used to calculate the sulfur concentration. This technique has a significant advantage over the IRMS technique that is limited to only isotope composition measurements.



**Major Accomplishments:** The international standards were measured for isotopic composition (Figures 1a – 1c) and concentration. The  $\delta^{34}\text{S}$  values (reported relative to VCDT ( $\delta^{34}\text{S} = -0.3$  ‰)) determined were  $-0.38 \text{ ‰} \pm 0.15 \text{ ‰}$  (1s),  $22.65 \text{ ‰} \pm 0.04 \text{ ‰}$  (1s), and  $-32.47 \text{ ‰} \pm 0.07 \text{ ‰}$  (1s) for IAEA-S-1, IAEA-S-2, and IAEA-S-3. Each standard showed less than 0.5 ‰ variability (IAEA-S-1  $\approx 0.4$  ‰, IAEA-S-2  $< 0.2$  ‰, and IAEA-S-3  $\approx 0.2$  ‰). The uncertainties are comparable to or better than those reported for IRMS the typical method used for isotope ratio analysis. Figures 1d – 1c show our (NIST/UMCP) results for the three standards relative to two other international labs, the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) and the Institute of Mineral Deposits (Beijing, China). These laboratories used a modified gas source (IRMS) mass spectrometer equipped with a molecular flow inlet system to determine the absolute isotope abundance ratios of the three standards. All labs obtained the same  $\delta^{34}\text{S}$  value for IAEA-S-1, the benchmark standard, and IAEA-S-2 within the uncertainties. This does not hold true for IAEA-S-3 where our values are the same as that obtained for the Beijing laboratory but is significantly different than the value obtained by IRMM. The value obtained by IRMM is also significantly different than that obtained by Beijing. This may potentially be due to scale contraction that is related to the gas source technique and which is eliminated by our technique. In each case our uncertainties are comparable or better than those obtained by the other labs. It is important to note that these measurements were made on samples ranging from 13  $\mu\text{g}$  to 65  $\mu\text{g}$ , which is smaller than the amounts used by the other laboratories (84  $\mu\text{g}$  to 125  $\mu\text{g}$ ). Our precisions on concentration measurements range from 0.07 % to 0.23 % (% rsd) which is comparable or an improvement over our present measurement capability (0.2 %) and includes a greater variability in the typical sample size taken for measurement.

**Impact and Future Plans:** The technique has shown considerable promise as a tool for the measurement of low concentration sulfate samples for both isotopic composition and concentration as demonstrated with standard measurements. The availability of TIMS instruments in laboratories around the world will make this technique immediately available to the scientific community and can be used for any applications requiring highly accurate and precise measurements of sulfur such as low-sulfur fossil fuels. We are presently in the process of applying this technique to low concentration snow and ice samples from Greenland and Krygstan. The data obtained will allow us to examine the degree of anthropogenic contribution to the sulfur cycle on a seasonal basis in these remote regions and to assess the spatial variability of global anthropogenic influence.

**Program:** Environmental Monitoring Technologies

**Title:** Developing Trace Analytical Methods and Gas Standards for Ammonia in Nitrogen

**Authors:** T.W. Vetter and W.J. Thorn

**Abstract:** NIST has been asked to develop a primary method for assigning ammonia concentrations to gas standards in the 1.0  $\mu\text{mol/mol}$  to 100  $\mu\text{mol/mol}$  range. These standards are of interest to the U.S. EPA for mobile and stationary source monitoring; and of interest to specialty gas mixture vendors who service these applications. Preliminary measurements were made this year evaluating three primary methods on a series of ten ammonia working standards from 5  $\mu\text{mol/mol}$  to 640  $\mu\text{mol/mol}$ . Ammonia concentrations for two of the working standards (40  $\mu\text{mol/mol}$  and 160  $\mu\text{mol/mol}$ ) were determined by a classical titrimetric method with relative expanded uncertainties of less than 1 %. All of the working standards were measured during an evaluation of a commercial ammonia instrument, which catalytically oxidizes ammonia to nitric oxide (>95 % efficiency) and then measures the nitric oxide by chemiluminescence. This method is of high interest because of the availability of a large quantity of nitric oxide primary standards in support of NIST SRMs. Additionally, all of the working standards were measured by FT-IR and a non-linear regression plot of the measured absorbances vs. concentration was developed. NIST has compared the ammonia values measured by the three analytical techniques and found that the 2 % to 4 % between the methods are difficult to resolve because the ten working standards of ammonia are decaying in concentration over time compared to their gravimetric preparation values.

**Purpose:** Natural gas turbines used to produce electric power generate significant  $\text{NO}_x$  and  $\text{SO}_x$  pollutants as emissions. Ammonia is added to the exhaust stream to neutralize the acid gases forming nitrate and sulfate salts, which are collected. The EPA regulations for continuous emission monitors (CEMs) require that ammonia not exceed 3  $\mu\text{mol/mol}$  excess in the stack emissions. Similarly, alternative fuels such as compressed natural gas (CNG) and hydrogen can generate ammonia in mobile source exhaust (cars and trucks), which must be monitored. Currently, there are no NIST SRMs or other reference materials available

### **Major Accomplishments:**

1. NIST ammonia in nitrogen working standards: A contract was issued to BOC Gases to produce 14 ammonia in nitrogen calibration gas standards by gravimetric dilution. An FT-IR spectrum was run on each of the 14 mixtures analyzed. A regression plot of the measured ammonia absorbances as a function of the ammonia concentration resulted in a non-linear FT-IR response curve. Seven of the 14 mixtures were returned to BOC.

2. Titration primary method for determining ammonia: The ammonia concentration was determined in two working standards whose nominal levels were at 40  $\mu\text{mol/mol}$  and 160 ppm.

The sample gas was metered into a solution of excess boric acid to form ammonium borate. The ammonium borate was neutralized by back titration with standardized hydrochloric acid to an original pH endpoint of the of the boric acid solution. The titrimetrically-determined mole fraction of ammonia in the two mixtures is  $(37.5 \pm 0.3) \mu\text{mol/mol}$  and  $(151.5 \pm 0.8) \mu\text{mol/mol}$ .

3. Oxidation of ammonia to nitric oxide and chemiluminescence analysis: NIST evaluated a commercial instrument, which oxidizes ammonia to nitric oxide and then measures the chemiluminescence response. The two highest working standards were diluted using NIST's Environics mass flow dilution system to generate ammonia reference mixtures similar to sample working standards being analyzed. Each of the working standards was assigned a concentration value, which was within 95 % of a similar NO response. The corresponding values for the two mixtures above are  $(39.1 \pm 0.8) \mu\text{mol/mol}$  and  $(155.7 \pm 0.8) \mu\text{mol/mol}$ . All of the measured values are observed to be 4 % to 6 % below the gravimetric blend values; suggesting that these working standards are unstable.

**Future Plans:** NIST will invest in the ammonia chemiluminescence instrument and attempt to link ammonia concentration determination to our primary Nitric Oxide gas standards. Work will also continue on the titrimetric method to provide direct linkage to the SI. Permeation systems will also be investigated in order to provide the conversion efficiency parameter for the chemiluminescence instrument.